



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/NL98/00321 <b>(22) International Filing Date:</b> 2 June 1998 (02.06.98) <b>(30) Priority Data:</b> 1006235 5 June 1997 (05.06.97) NL 1007333 23 October 1997 (23.10.97) NL <b>(71) Applicant (for all designated States except US):</b> DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> SCHERRENBERG, Rudolf, Lucien [NL/BE]; Kruisstraat 11, B-3530 Houthalen-Helchteren (BE). SMELT, Harold, Jan [NL/NL]; Felix Ruttenstraat 67, NL-6132 CW Sittard (NL). DE VOS, Roelof, Franciscus, Gerardus, Maria [NL/NL]; Prinses Beatrixstraat 9, NL-6241 EW Meerssen (NL). <b>(74) Agent:</b> NIEUWKAMP, Johannes, Gerardus, Maria; Octrooi- bureau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).		<b>(81) Designated States:</b> AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GE, HU, ID, IL, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, SL, TR, TT, UA, US, UZ, VN, YU, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> PROCESS FOR PREPARING POROUS POLYOLEFIN PARTICLES		
<b>(57) Abstract</b> <p>The invention relates to a process for preparing porous polyolefin particles. The process according to the invention is characterized in that it comprises the following steps: 1) dissolving at least one crystallizable polyolefin in a solvent, in the absence of a nucleating agent; 2) dispersing the polyolefin solution obtained in a non-solvent in the presence of a surfactant, at a temperature that is higher than the crystallization temperature of the polyolefin in the polyolefin solution; 3) cooling the multi-phase system obtained with stirring, at a rate of between 0.05 and 10 °C/min to a temperature that lies below the crystallization temperature of the polymer in the polymer solution, so that firm polyolefin particles are formed; 4) separating the polyolefin particles; 5) drying the polyolefin particles. The invention also relates to a porous polyolefin particle with a high effective loadability and a narrow particle size distribution.</p> <div data-bbox="743 1203 1344 1696" data-label="Image"> </div> <p style="text-align: center;">SEM photograph of a porous polyolefin particle with a narrow DOD at a magnification of 18x (Example 1).</p>		

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PROCESS FOR PREPARING POROUS  
POLYOLEFIN PARTICLES

10 The invention relates to a process for preparing porous polyolefin particles.

Such a process is known from EP 0 370 260 A1. The drawback of the process described therein is however that a large number of different liquids is required to be able to prepare the porous polymer particles. First a mixture of (at least) two liquids is used to dissolve the polymer, for which a high temperature is required. This results in the formation of a homogeneous polymer solution. Then a third liquid (a hot, inert dispersing agent) is added to the polymer solution obtained. This results in a two-phase system. This two-phase system is vigorously stirred, which results in the formation of droplets of the polymer solution. Then a fourth, cool inert liquid is added. Next, the droplets are collected and finally an extraction step takes place. Another fifth liquid at least is required for the extraction. In some cases the extraction has to be followed by washing with yet another (at least sixth) liquid, as appears from Example 11. As a large number of liquids is required in the known process, on an industrial scale it results in many waste streams which have to be purified. From an environmental and process technological viewpoint this process is unsatisfactory and therefore there is a need for a better process.

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The invention's aim is to provide a process for preparing porous polyolefin particles with which the aforementioned drawback is entirely or partly eliminated. This aim is achieved because the process  
5 comprises the following steps:

- 1) dissolving at least one crystallizable polyolefin in a solvent, in the absence of a nucleating agent, which results in the formation of a polyolefin solution,
- 10 2) dispersing the polyolefin solution obtained in a non-solvent in the presence of a surfactant, at a temperature that is higher than the temperature at which the polyolefin in the polyolefin solution starts to crystallize, which results in the  
15 formation of a multi-phase system,
- 3) cooling the multi-phase system obtained, with stirring, at a rate of between 0.05 and 10°C/minute to a temperature that lies below the crystallization temperature of the polymer in the  
20 polymer solution, so that firm polyolefin particles are formed,
- 4) separating the polyolefin particles,
- 5) drying the polyolefin particles.

This ensures that fewer (different) liquids  
25 are required in the process according to the invention, direct consequences of which are that fewer waste streams have to be purified and that the process is easier to carry out than the process described in EP 0 370 260 A1. The process according to the invention  
30 moreover involves a smaller risk of the porous polyolefin particles prepared containing remains of one or more of the liquids. An advantage of the process of the present invention, moreover, is that the dimensions of the porous polyolefin particles are better

controllable. Another advantage is that the dimensions of the porous polyolefin particles prepared show a smaller spread than in the state of the art.

A process for preparing polymer particles with controllable dimensions is known from EP 0 644 230 A1, but no indication whatsoever is given herein of how porous polymer particles are to be made.

The porous polyolefin particles obtained by using the process according to the present invention can be prepared using as starting materials a wide variety of polyolefins. Homopolymers are suitable, but so are copolymers. The term 'copolymers' is here and hereafter understood to mean polymers composed of two or more different monomers. The monomers to be used may be  $\alpha$ -olefins (such as ethylene, propylene or other  $\alpha$ -olefins with 4-12 C atoms). The monomer may also be of a polar nature, such as for instance vinyl acetate. The advantage of a vinyl acetate as a comonomer is that the porous particle made thereof is better capable of absorbing polar substances. The concentration of polar monomer, for example vinyl acetate in EVA (ethylene-vinyl acetate copolymer), suitable for the preparation of porous particles, is at most 25 wt.% relative to the total amount of polymer. In the context of the invention it is also possible to use mixtures of different polyolefins.

The polyolefins that can be used may be both freshly prepared polyolefins and polyolefins obtained after upgrading of used materials, for example in the framework of recycling, polyolefins collected as production rejects and production waste, contaminated polyolefins and polyolefins that do not meet previously specified product requirements, i.e. off-spec products.

It is important that the polyolefins are soluble at a particular temperature and that the polyolefin is crystallizable, so that solid, porous structures are formed in the cooling step. It is  
5 however not necessary for the polyolefin to be completely (100%) crystallizable.

Polyolefins that are suitable for preparing the porous polyolefin particles according to the invention are for example polyethylene, polypropylene,  
10 polybutylene, poly(4-methyl-1-pentene), polycyclohexylethylene. Preferably use is made of polyethylene and/or polypropylene, more preferably use is made of polyethylene. It is not critical what type of polyethylene is used in the process according to the  
15 invention. The polyethylene may for example have been prepared via processes known per se, including solution, slurry, gas-phase and high-pressure processes. The polyethylene's density may vary between 880 and 965 kg/m<sup>3</sup>. Use can for example be made of ultra-  
20 high-molecular-weight polyethylene (UHMWPE), high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), low-density polyethylene (LDPE), very-low-density polyethylene (VLDPE) and ultra-low-density polyethylene (ULDPE). Preferably use is made of  
25 LDPE or LLDPE.

'LLDPE' is understood to be a substantially linear homopolymer or copolymer of ethylene and one or more  $\alpha$ -olefins with 3-12 C atoms and optionally one or more non-conjugated dienes. Particularly suitable  $\alpha$ -  
30 olefins are propylene, 1-butene, 1-hexene, 4-methylpentene-1 and 1-octene. Suitable dienes are for example 1,7-octadiene and 1,9 decadiene. LLDPE mainly has short side chains of 1 to 10 C atoms and considerably shorter side chains than LDPE.

LDPE is a highly branched polyethylene. As LDPE use can be made of for example polyethylene that is produced in the usual way in a high-pressure process with the aid of one or more radical initiators. This  
5 high-pressure process can take place in an autoclave or in a tubular reactor. LDPE has a density lower than 935 kg/m<sup>3</sup>. Mixtures with EVA are also very suitable.

When polypropylene is used, both isotactic and syndiotactic polypropylene may be used. Copolymers  
10 of propylene and one or more other  $\alpha$ -olefins, for example ethylene and butylene, are also possible.

In the preparation of the porous polyolefin particles use can be made of one polyolefin or of a mixture of polyolefins. If use is made of one  
15 polyolefin, this polyolefin preferably has a DSC crystallization peak with a width of at least 5°C. Preferably the width of the crystallization peak is at least 10°C and in particular at least 15°C. This width is the peakwidth measured at half of the height of the  
20 crystallization peak in the DSC curve.

When a mixture of polyolefins is used, these polyolefins must preferably have different crystallization peak temperatures. Preferably such a difference in crystallization temperatures is 5°C or  
25 more. The amount of polyolefin with a higher crystallization temperature is at least 0.1 wt.% relative to the polyolefin with a lower crystallization temperature, preferably between 1 and 5 wt.%.

Preferably the polyolefins or mixtures of  
30 polyolefins show a fast crystallisation behaviour upon cooling of the polyolefin solution. Crystallisation behaviour is considered to be fast, when the maximum crystallisation peak lies within 5 °C of the start of

crystallisation in a DSC experiment as indicated hereinafter.

A polyolefin's crystallization temperature and thermal behaviour can be determined with the aid of the Differential Scanning Calorimetry (DSC) technique.

In a DSC measurement a substance or a mixture of substances is heated or cooled under controlled conditions in a controlled atmosphere while the difference in temperature between the substance and a reference material (as a result of energy changes in the substance) is continuously measured. A transition (such as melting or crystallization) is marked by the substance or the mixture absorbing or releasing energy, which results in a corresponding endothermal or exothermal peak in the DSC curve. As already mentioned above, the curve may contain more than one peak.

A DSC measurement can be carried out both on the polyolefin and on the solution of the polyolefin in the solvent.

For the DSC measurements in the context of the present invention the polyolefin or the polyolefin solution is heated at 5°C/min. to 200°C (first heating curve); this is followed by cooling by 5°C/min. to -50°C (cooling curve). Then a second heating curve is recorded at a heating rate of 5°C/min. The polyolefin's melting and crystallization behaviour is characterized on the basis of the latter two curves. Of course allowance must be made for the fact that crystallization/melting of the solvent may also be observed in the DSC measurement, which should not be confused with the polyolefin's DSC behaviour.

The temperature at which the (DSC) crystallization curve (the cooling curve) deviates 1% from the base line is taken as the temperature at which



crystallization starts, the percentage being relative to the height of the maximum peak. The width of the crystallization peak is defined as the width at half height at the temperature at which the cooling curve  
5 shows a maximum.

The process of the invention is carried out in the absence of a nucleating agent. Here and hereinafter a nucleating agent is an ingredient which has an ability to stimulate the formation of polyolefin  
10 crystallites during the cooling of the polyolefin solution and does not dissolved in the polyolefin solution during the process of the invention.

The polymer particle is dried at a temperature at which a substantial portion of the  
15 crystallization of the polyolefin has already taken place. Preferably the drying temperature is below the temperature in the DSC thermogram at which 50% of the polyolefin's total heat of crystallization has been released. The heat of crystallization is represented by  
20 the surface area beneath the cooling curve in the DSC thermogram. Preferably the drying temperature is lower than the temperature at which 75% of the total heat of crystallization has been released. This ensures that the porous polyolefin's structure remains optimally intact  
25 during the drying process.

The process according to the invention is carried out as follows. The polyolefin or the mixture of polyolefins is first dissolved in a solvent. Various organic liquids can be used as the solvent. The type of  
30 solvent to be used will to a great extent depend on the solvent's ability to dissolve the polyolefin. Suitable organic solvents for use in the process of the present invention are for example compounds from the series of the n-alkanes, i-alkanes, cycloalkanes, polycyclic

compounds with two or more cyclic structures, alkenes, cycloalkenes, aromatic compounds which may or may not be substituted, chlorinated hydrocarbons, decalin, tetralin or paraffin oil. Mixtures hereof are also  
5 suitable. The compounds may be both substituted and unsubstituted. The substituent group may consist of both C and H atoms alone, and of C, H and/or hetero atoms. The substituent group preferably has 3-100 C atoms. Preferably use is made of n-alkanes, i-alkanes,  
10 cycloalkanes, aromatic compounds which may or may not be substituted and decalin or mixtures thereof. When polyethylene is used as the polyolefin use is in particular made of a cycloalkane or an alkane, more in particular of cyclohexane, boiling-point spirit,  
15 hexane, heptane or octane or mixtures thereof. Usually a polar solvent is used for polar olefins.

The polyolefin can optionally be dissolved in the solvent with simultaneous heating. If necessary, the dissolving can be accelerated by means of dynamic  
20 or static mixing. In some cases, depending on the type of solvent chosen, it may be advantageous to work at elevated pressure, which enables dissolution at a temperature above the solvent's atmospheric boiling point. A person skilled in the art will easily be able  
25 to determine whether working at elevated pressure will be advantageous. The temperature at which the polyolefin is dissolved is not critical as long as the polyolefin dissolves. A person skilled in the art will be able to easily determine this, too. Usually the  
30 dissolution temperature will lie between 40 and 200°C. Preferably the dissolution temperature lies between 70 and 180 °C. Under these conditions the polyolefin is effectively dissolved in the solvent.

Generally use is made of an amount of solvent such that the polyolefin solution that is formed contains between approx. 0.1 and 50 wt.%, preferably between 15 and 35 wt.%, polyolefin. This obviates the need for interim removal through evaporation of part of the solvent. At concentrations of > 50 wt.% it becomes difficult to stir the polyolefin solution; at low concentrations the process becomes less interesting from an economic viewpoint.

10 The polyolefin solution obtained and a non-solvent are dispersed in one another, optionally with stirring or a different form of dynamic or static mixing. The order in which the non-solvent and the polyolefin solution are added to one another for  
15 dispersion is not critical, provided the non-solvent is the continuous phase in the dispersion obtained. The non-solvent is a compound in which the polyolefin does not dissolve. For the term 'non-solvent' reference is made to the tables presented in 'Polymer Handbook', J.  
20 Bandrup and E.H. Immergut, eds., John Wiley and Sons, 3rd Ed. (1989), pp. VII/379 and following. The amount of non-solvent to be used is not critical, provided that the non-solvent remains the continuous phase in the dispersion obtained. The polyolefin solution : non-  
25 solvent volume ratio may vary between 10:1 and 1:10; preferably this ratio varies between 5:1 and 1:5. Most preferably the ratio varies between 1:1 and 1:3.

The non-solvent is a polar or an apolar compound, depending on the polyolefin's polarity. A  
30 polar non-solvent is very suitable for use with a polyolefin that dissolves in an apolar solvent. Polar compounds that are suitable for use as non-solvent are for example water or a compound from the group of the organic or inorganic acids, ketones or alcohols.

Preferably water, acetone, methanol or ethanol are used and more preferably water is used. Mixtures of these compounds are also suitable.

During dispersion of the polyolefin  
5 solution in the non-solvent a multi-phase system is formed, a 'multi-phase' system being understood to be a system that consists of at least two phases, one of which contains the polyolefin: the polyolefin-containing phase. During dispersion of the polyolefin  
10 solution and the non-solvent the temperature of the polyolefin solution and the non-solvent must lie above the temperature at which the polyolefin in the polyolefin solution starts to crystallize. Preferably the temperature lies at least 15°C above the temperature  
15 at which crystallization starts.

To control the dispersion's dimensions, and hence the ultimate size of the porous polyolefin particles to be obtained, it is necessary to add a surfactant to the non-solvent. The higher the  
20 concentration of surfactant, the smaller the particles and vice versa. The surfactant concentration is preferably between 10 ppm and 5 wt.%, more preferably between 100 ppm and 1 wt.%. If the surfactant concentration is too low, the droplets of polyolefin  
25 solution may show too great a tendency to aggregate. If the surfactant concentration is too high, very small particles may be formed. By using the process of the present invention, porous polyolefin particles with dimensions from 0.01 up to approximately 12 mm can be  
30 obtained. An average person skilled in the art will easily be able to experimentally determine the most desirable concentration.

The surfactant may be an anionic, cationic, non-ionic or amphoteric tenside. Suitable surfactants

are for example compounds from the group of the alkane sulphonates, alkylbenzene sulphonates, fatty alcohol sulphonates, alkylammonium compounds, tensides of the betaine type, alkyl polyglycol ethers, ethoxylated  
5 fatty amines, Tween®, Span® and alkyl phenol ethoxylates.

If the presence of one or more surfactants results in foam formation, an anti-foaming and/or defoaming agent can be added. A combination of anti-  
10 foaming and/or defoaming agents is also possible. These anti-foaming and/or defoaming agents can be added in different steps of the process, but preferably before the dispersion step.

In the process according to the invention,  
15 for example during or after step 2, a portion of the solvent can optionally be evaporated from the multi-phase system formed. Whether evaporation is necessary or not will depend on the polyolefin and the solvent used as the starting materials and the initial  
20 polyolefin concentration. The amount of solvent to be evaporated depends on the polyolefin solution's concentration. The lower the concentration, the greater the amount that can be evaporated.

The solvent, the non-solvent and the  
25 polyolefin (mixture) can also be combined in a single step. This mixture is then stirred, optionally with heating, until the polyolefin has dissolved and the polyolefin solution has been dispersed in the non-solvent. The resulting multi-phase system is  
30 subsequently cooled.

The cooling of the multi-phase system in the process according to the invention (step 3) takes place at a rate between 0.05 and 10°C/minute, preferably at a rate between 0.1 and 5°C/min and in particular

between 0.2 and 2°C/min. This cooling is in principle continued until more than 50% of the total heat of crystallization of the polyolefin in the polyolefin solution has been released. The temperature

5 corresponding to this point can, as already described above, be determined with the aid of the DSC technique.

If the temperature is still too high, the polyolefin particles are too soft to be efficiently separated. If this phenomenon occurs, deeper cooling  
10 will be required. When cyclohexane and/or n-heptane are/is used as a solvent for polyethylene as the polyolefin, the cooling is preferably continued to below 40°C. When polypropylene is applied as the polyolefin, the cooling is preferably continued to  
15 below 70°C.

The dispersion must be retained during the cooling of the multi-phase system, which can be realized with the aid of stirrers or by means of static or dynamic mixing. The particle size can also be  
20 controlled depending on the type of stirrer and the speed. The higher the amount of energy supplied, or the more vigorous the stirring (with the same type of stirrer), the smaller the porous polyolefin particles will be. And, vice versa, the lower the amount of  
25 energy supplied, or the slower the stirring, the larger the particles will be.

Next, the polyolefin-containing particles are separated from the multi-phase system (step 4). This separation can take place in a manner known to a  
30 person skilled in the art. Suitable techniques are for example vacuum filtration, centrifugation and/or filtration pressing. Preferably use is made of filtration under the influence of gravity.

In step 5) the separated polyolefin particles, which still contain solvent and optionally non-solvent, are dried. Drying may take place to any desired degree of solvent and non-solvent removal. The execution of this drying process largely determines whether or not the polyolefin particles obtained will retain their porosity. The drying process for obtaining porous polyolefin particles can be carried out in various ways, both as such or in combination with each other. The drying can for example take place under reduced pressure, the polyolefin-containing particles can be stripped with a gas or vapour or the polyolefin-containing particles can be dielectrically dried (for example with the aid of microwave or RF (radio-frequency) drying as for example described in 'Microwave Processing and Engineering', R.V. Decareau and R.A. Peterson, ed. Ellis Horwood Ltd and VCH GmbH, 1986, or in 'Industrial Microwave Heating', A.C. Metaxas and R.J. Meredith, Peter Peregrinus Ltd., 1983).

Suitable gases for use in the stripping process and optionally during drying under reduced pressure are for example air, nitrogen, helium, carbon dioxide and methane. Preferably nitrogen is used as the stripping gas.

The drying, also under reduced pressure, preferably takes place under conditions such that the partial pressure of the solvent in the vapour phase is less than 50%, but more preferably less than 20%, of the solvent's normal vapour pressure at the drying temperature.

The temperature during the drying of the polyolefin particles is initially preferably below the temperature at which 75% of the total heat of

cystallization has been released. This temperature can be determined with the aid of DSC. The drying temperature may be increased higher as the amount of solvent decreases and as a result the polyolefin's concentration increases. Especially the removal of the non-solvent may need a higher drying temperature to be effectively carried out. When polyethylene is used as the polyolefin the drying is preferably initially carried out at a temperature below 30°C; preferably this temperature is below 20°C.

Irrespective of the type of drying process chosen, the drying preferably takes place under conditions such as to prevent disintegration of the particle structure as much as possible (for example by capillary and mechanical forces). Disintegration of the particle structure will cause the particle size distribution to increase. The particle size distribution will hereinafter be quantified by the degree of dispersion (DOD). A person skilled in the art will easily be able to determine in one or more experiments whether any disintegration of the particle structure takes place.

In a preferred embodiment of the process according to the invention use is made of specific non-ionic tensides as surfactants. Typical examples of the specific non-ionic tensides are tensides from the group comprising alkyl polyglycol ethers, ethoxylated fatty amines or alkyl phenol ethoxylates. Most preferably use is made of alkyl polyglycol ethers or ethoxylated fatty amines. The use of these non-ionic tensides in the preparation of porous polyolefin particles surprisingly results in particles with a very small DOD.

The advantage of using the aforementioned specific non-ionic tensides is not restricted to a



process which is carried out in the absence of a nucleating agent. Comparable advantages can be obtained, when a nucleating agent is present in a further analogous process for the preparation of porous polyolefin particles.

The particle size distribution is quantified by the degree of dispersion (DOD), as determined according to DIN 66 165. An advantage of the porous polyolefin particles that have a small DOD is that their flow behaviour has been greatly improved and that the porous polyolefin particles thus prepared can be very accurately, and in a reproducible manner, dosed to processing machines like extruders. The particles obtained with the process in which the specific non-ionic tensides are applied according to this invention have a DOD of  $< 0.4$ . Particles with such a small DOD are not yet known to date. The invention therefore also relates to these porous polyolefin particles.

The porous polyolefin particles according to the invention have:

A) a porosity ( $\epsilon$ ) of 5-85%

B) an effective loadability,  $E_{1A}$ , of at least 95%, where

$$E_{1A} = \frac{\frac{\frac{m_A}{\rho_A}}{\frac{m_A}{\rho_A} + \frac{m_{PO}}{\rho_{PO}}} * 100\%}{\text{porosity}}$$

35

C) an absorption time ( $t_a$ ) of at most 10 minutes

D) a DOD of less than 0.4,

where  $E_{1A}$  is the effective loadability of the polyolefin particle with an absorption agent,  $m_A$  the absorbed weight of the absorption agent,  $\rho_A$  the absorption agent's density,  $m_{po}$  the weight of the porous polyolefin particles before absorption of the absorption agent,  $\rho_{po}$  the polyolefin's density.

These porous polyolefin particles have an accessible open pore structure and a narrow particle size distribution. These particles have a high effective loadability, a short absorption time, are suitable for use as concentrate and show good flow and dosing properties.

A suitable absorption agent for determining the effective loadability is Atmer<sup>®</sup> 163, an ethoxylated amine.

The particles' porosity  $\epsilon$  is determined with the aid of mercury (Hg) porosimetry according to ASTM-standard D4284-83 using an Autopore II 9220 from Micrometrics (USA). The porosity is determined by measuring the volume of Hg that is forced into the pores at various pressures. The measurement starts at a pressure 3kPa. At this low pressure the open spaces between the polyolefin particles are '(inter)' filled with Hg. Subsequently the pressure is continuously increased upto about 400 MPa, resulting in intrusion of Hg into the polyolefins particles '(intra)'. At high pressures some compression of the polymeric material might occur. The difference between the volume of Hg in the dilatometer before and after pressurization is a measure for the porosity of the polyolefin. The porosity is calculated by dividing the intruded-Hg-volume determined at the pressure at which 85% of the pores are filled minus the intruded-Hg-volume determined at a pressure at which 15% of the pores are

filled by the total volume of the porous particle. The total volume of the porous particle is calculated by summarizing the intruded Hg-volume as specified above with the weight of the polymer sample divided by its density. The particles porosity varies between 5 and 85%. Preferably the porosity is more than 25%, more preferably more than 35%. A high porosity results in a wide range of possible applications for the porous polyolefin particle. The pore diameter varies between 0.01 and 100  $\mu\text{m}$ .

To determine the effective loadability, a weighed amount of porous particles is introduced into a beaker with a stirring bar at room temperature. A certain amount of absorption agent, such as Atmer<sup>®</sup> 163, is added with stirring until the porous particles no longer absorb any absorption agent. This is the case when a film of liquid and/or droplets of Atmer<sup>®</sup> is/are formed on the beaker's wall which has/have still not disappeared after 5 minutes. The porous polyolefin particles are then considered to be saturated with the absorption agent. By now weighing the porous particles again, the amount of absorption agent absorbed can be determined. With the porous polyolefin particles according to the invention  $E_{1A}$  is  $> 95\%$ , preferably  $> 99\%$ .

A major advantage of the porous polyolefin particles according to the invention is that the particles can absorb a large amount of absorption agent and that, moreover, this absorption process also proceeds rapidly. The absorption time of the porous polyolefin particles according to the invention is at most 10 minutes. The absorption time ( $t_a$ ) is determined by filling a beaker with DOW Corning 200<sup>®</sup> Fluid, viscosity 1 cSt at  $R_t$ , density 820  $\text{kg/m}^3$ . The porous

polyolefin particles are placed on top of this liquid. The absorption time is the amount of time the particles require to sink to the bottom of the beaker. All this takes place at room temperature.

5                   The DOD is determined using a non-sieved polyolefin, by means of an experiment for determining the particle size. The particle size is determined according to standard DIN 66 165.

                  The DOD is defined as:

10

$$\text{DOD} = (d_{84} - d_{16}) / 2d_{50}$$

where  $d_{xx}$  indicates the mesh-size of a sieve at which  $xx$  wt% of the porous polyolefin particles fall through the sieve. A high DOD points to a wide particle size distribution. A small DOD points to a narrow particle size distribution and is favourable for the flow, dosing and mixing properties of the porous polyolefin particles.

20                   The porous polyolefin particles of the invention have a DOD of  $< 0.4$ . Preferably the DOD is  $< 0.2$ . More preferably the DOD is  $< 0.15$ .

                  The size of the porous polyolefin particles according to the present invention ( $d_p$ ) usually varies between 0.5 and 12 mm. Particles that are smaller than 0.5 mm and larger than 12 mm are also possible, but the dosing properties and flow properties are then less favourable.

30                   By way of illustration, a few electron microscopy (SEM) photos of porous polyolefin particles obtained by using the process according to the invention are shown in Figures 1-4. Figure 5 shows porous polyolefin particles with a narrow DOD, while figure 6 shows polyolefin particles with a wide DOD.

The porous polyolefin particles prepared with the process according to the invention are suitable for different applications, for example as concentrates, absorbents or carriers of substances that are to be released slowly and/or in a controlled manner.

To ensure good dispersion of additives, for example auxiliary materials, accessory agents, reagents, product and process conditioners, in a plastic it is advantageous and sometimes necessary to add the additives to the plastic in the form of a concentrate of the additives in a polymeric matrix. Concentrates, for example, are often used in plastics as so-called masterbatches. To ensure economic use of the additives it is advantageous for the additive in the polymeric matrix of the masterbatch to have the highest possible concentration. However, especially in the case of liquid additives, it often proves impossible to ensure good dispersion of high concentrations of the additives in the polymeric matrix. Porous polyolefin particles are particularly suitable for absorbing high concentrations of one or more additives. In the case of liquid additives the additive can be directly absorbed. If the additive is in a solid form, it can be melted, dissolved or dispersed in a suitable liquid before being brought into contact with the porous polyolefin particle. The absorption of additives in the porous polyolefin particle can be effected according to known techniques. A suitable technique is for example to dose the additive to the porous polyolefin particle in a powder mixer.

A concentrate is often mixed with another polymer, for example a polyolefin, in an extruder so

that the additive is homogeneously distributed in the polymer. The porous polyolefin particle (prepared according to the process of this invention) is eminently suitable for mixing with another polymer, for example a polyolefin, in mixing equipment, such as for example an extruder. This is because the porous particle has a balanced mechanical stability. In a simple powder mixer the porous particle's structure will remain almost entirely intact, so that little or no dust is formed during the forming of the concentrate. When this concentrate is mixed with a polymer in an extruder, the porous concentrate is crushed under the influence of the universal pressure prevailing in the extruder's solids transport zone, so that a good dispersion of the concentrate over the polymer is achieved even before the polymers have been melted. No high demands need then be imposed on the mixing of the polymer melt. Use can therefore be made of a simple extruder, for example a single-screw extruder, or the extrusion can be effected with high throughputs, because only few pressure-consuming mixing elements are required in the extruder to ensure good mixing.

In another application of these porous polyolefin particles according to the invention the particles can be used to effect a slow release of an active substance. To this end the active substance is first absorbed by the porous polyolefin particle, after which the substance in question is slowly released. Medicines, fragrances, insecticides, pheromones and fertilizers can be mentioned as examples of active substances.

The porous polyolefin particles are also suitable for (selectively) absorbing certain

substances. Examples are the absorption of stench components, leaked and/or spilled liquids or the purification of contaminated water streams, in which process the porous polyolefin particle absorbs the  
5 contaminants. The use of polar, porous polyolefin particles, such as EVAs, ensures that the particles are well capable of absorbing polar substances.

The invention will be further elucidated with reference to the following Examples without being  
10 limited thereto.

In the Examples the density,  $d$ , was determined according to ASTM standard D792-66. The melt index, MI, was determined according to ASTM standard D1238, condition E.

15 The DSC measurements were carried out using a Perkin-Elmer DSC-7. The temperature and energy calibrations were carried out on the basis of the melting of indium and lead. The temperature measurement during the cooling is controlled on the basis of the  
20 solid-solid transition of 4,4'-azoxy-anisole. Heating and cooling rates of 5°C/min. were used during the measurement.

The results of the measurements of the Examples are given in Table 1.

25

#### Example I

In an Erlenmeyer flask 60 grams of LDPE (with a density of 918 kg/m<sup>3</sup> and an MI of 8 dg/min.) was dissolved in 190 grams of heptane at approx. 95°C with  
30 reflux. 0.6 grams of LLDPE (with a density of 936 kg/m<sup>3</sup> and an MI of 4.4 dg/min.) was added to this solution and dissolved. Next, the solution obtained was dosed to a vessel containing 500 grams water of approx. 74°C with 0.4 grams of non-ionic surfactant, a C<sub>11</sub>-oxo alcohol

polyglycol ether with 7 ethylene oxide units. With stirring with the aid of a pitched-blade stirrer (200-300 W/m<sup>3</sup>) and a continuous nitrogen flow of 10 litres/hour, while the temperature was kept constant at 78°C, the water and the polyolefin solution were dispersed for 5 minutes and then cooled to room temperature at a cooling rate of approx. 1°C/min. Then the particles were separated with the aid of a sieve. This resulted in firm, predominantly spherical, wet polyolefin particles with a d50 of 1.85 mm. These particles were then dried in a vacuum stove at room temperature and a pressure of < 10 kPa. The structure of the polymer particles has been visualized with scanning electron microscopy (SEM) scans. Magnifications of the porous polyolefin particles of 80\*, 500\*, 1000\* and 2000\* are shown in figures 1 to 4 respectively. The figures show an open pore structure with interconnecting cells. The narrow particle distribution has been shown in figure 5: the particles have a rather uniform size.

#### Example II

Polyolefin particles were prepared according to Example I. 0.4 grams of isotridecyl alcohol polyglycol ether with 8 ethylene oxide units was used as the non-ionic surfactant.

#### Example III

Example II was repeated using 0.6 g of non-ionic surfactant. Firm, predominantly spherical polyolefin particles were obtained.



Comparison of Examples II and III shows that the porous polyethylene particles become smaller when the concentration of non-ionic surfactant is increased.

#### 5 Example IV

In an Erlenmeyer flask 80 g of LDPE (with a density of 918 kg/m<sup>3</sup> and an MI of 8 dg/min.) was dissolved in 190 g of heptane at approx. 95°C with reflux. 0.8 g of LLDPE (with a density of 936 kg/m<sup>3</sup> and  
10 an MI of 4.4 dg/min.) was added to the solution and dissolved. The solution was dosed to a vessel containing 580 g of water of 74°C to which 0.4 g of C<sub>11</sub>-oxo alcohol polyglycol ether with 7 ethylene oxide  
15 units had been added as a non-ionic surfactant. This was followed by stirring and cooling as described in Example I. The polyolefin particles were separated with the aid of a sieve. These particles were dried in a fluid bed with a nitrogen flow of 40°C.

A higher concentration of polyolefin in the polyolefin  
20 solution results in a porous polyolefin particle with a lower porosity.

#### Example V

In a vessel 85 g of LDPE (with a density of  
25 918 kg/m<sup>3</sup> and an MI of 8 dg/min.) was dissolved in 300 g of heptane at 95°C with heptane reflux. 0.85 grams of LLDPE (with a density of 936 kg/m<sup>3</sup> and an MI of 4.4 dg/min.) was added to the solution. Next, 750 grams of water of 74°C in which 0.6 g of non-ionic surfactant,  
30 C<sub>11</sub>-oxo alcohol polyglycol ether with 7 ethylene oxide units, had been dissolved was dosed to this solution. The rest of the preparation was carried out as in Example I.

Example VI

In a vessel 11 kg of LLDPE (with a density of 918 kg/m<sup>3</sup> and a melt index of 8 dg/min.) and 0.1 kg of LLDPE (with a density of 936 kg/m<sup>3</sup> and a melt index of 4.4 dg/min.) were in 30 minutes dissolved in 35 kg of heptane at approx. 95°C. With stirring, with a power supply of approx. 1000 W/m<sup>3</sup>, the solution was dosed to a vessel containing 125 litres of water of approx. 80°C to which 0.125 kg of a non-ionic surfactant (C<sub>11</sub>-oxo alcohol polyglycol ether with a chain consisting of 7 ethylene oxide groups) had been added. The stirring configuration consisted of MIG stirrers combined with 4 baffles. The pressure increased because the heptane/water mixture reached its azeotropic boiling point. After the addition of the organic phase the mixture was cooled at a rate of approx. 1°C/min. After the mixture was cooled to 30°C it was poured onto a sieve to separate the water phase. After separation predominantly spherical polyolefin particles with a diameter of 3 to 4 mm remained. These particles were subsequently dried in a continuously vibrated fluid bed with nitrogen circulation, the ingoing fluidizing gas having a temperature of 40-60°C. The bed temperature increased slowly from 5 to 60°C.

The porous polyolefin particles showed comparable characteristics as the particles made in Example I.

Example VII

Example VI was repeated, but now 37 kg of cyclohexane was used. The particles were dried in a tray drier, inertized with nitrogen, at a pressure of < 10 kPa and a plate temperature of 20 °C. After about 48 hours the plate temperature was increased to 50 °C.

Example VIII

190 g of n-heptane, 60 g of LDPE with a density of 918 kg/m<sup>3</sup> and an MI of 8 dg/min., 0.6 g of LLDPE with a density of 936 kg/m<sup>3</sup> and an MI of 4.4 dg/min. and a soap solution were introduced into a vessel. The soap solution consisted of 580 g of demineralized water and 0.40 g of C<sub>11</sub>-oxo alcohol polyglycol ether with 7 ethylene oxide units. The mixture obtained was inertized with nitrogen and heated to 95°C with stirring with the aid of a pitched-blade stirrer (200 W/m<sup>3</sup>). After the stirrer had been stopped, complete phase separation was awaited. The two-phase system was subsequently cooled with stirring to 25°C at 1°C/min. After the polyolefin particles had been separated with the aid of sieve, firm, predominantly spherical particles were obtained. These particles were dried in a vacuum stove at room temperature and a pressure of < 10 kPa.

20 Example IX

Example VIII was repeated, only now the LDPE employed had a density of 932 kg/m<sup>3</sup> and an MI of 8 dg/min.

25 Example X

17 g of polypropylene with a density of 904 kg/m<sup>3</sup> and an MI of 19 dg/min. was dissolved in 190 g of p-xylene at 130°C in an Erlenmeyer flask. The solution obtained was then dosed to a vessel containing a soap solution with a temperature of 90°C. The soap solution consisted of 780 g of demineralized water and 2.0 g of fatty alcohol polyglycol ether with 9 ethylene oxide units. The mixture obtained was inertized with nitrogen. The water and the polyolefin solution were

dispersed for 5 minutes with stirring with the aid of a pitched-blade stirrer (250 W/m<sup>3</sup>) and then cooled to 25°C at 1°C/min. The particles formed were then separated from the water with the aid of a sieve. Firm, predominantly spherical, wet polyolefin particles were obtained. These particles were then dried in a fluid bed with the aid of a flow of nitrogen, the temperature of the drying gas being varied from 5 to 40°C. During the evaporation of the solvent the temperature of the product did not rise above 20°C. The porosity was 77%.

#### Comparative experiment A

In an Erlenmeyer flask 60 grams of LDPE (with a density of 918 kg/m<sup>3</sup> and an MI of 8 dg/min.) was dissolved in 190 grams of heptane at approx. 95°C with reflux. The solution was then cooled to 80°C and subsequently dosed to a vessel containing 500 g of water of approx. 74°C, to which 0.4 g of surfactant (an alkane sulphonate with an average chain length of 14.5 C atoms) had been added. With stirring with the aid of a pitched-blade stirrer (250 W/m<sup>3</sup>) and a continuous nitrogen flow of 10 litres/hour, while the temperature was kept constant at 78°C, the polyethylene solution was dispersed in the water for 5 minutes and then cooled to room temperature at a cooling rate of approx. 1°C/min. Then the particles were separated with the aid of a sieve. This resulted in firm, predominantly spherical, wet gel particles. These particles were subsequently dried in a vacuum stove at room temperature and a pressure of < 10 kPa).

Porous polyolefin particles are formed which show a very broad particle size distribution (see figure 6).

Comparative Experiment B

158 grams of n-heptane, 52 grams LDPE with a density of  $926 \text{ kg/m}^3$  and an MI of 4 dg/min, 0.6 gram di-ethylbenzylidene sorbitol (the product NC-4 supplies by Mitsui Toatsu) and a soap solution were introduced into a vessel. The soap solution consisted of 580 gram of demineralized water and 0.4 gram of  $\text{C}_{11}$ -oxo alcohol poly glycolether with 7 ethylene-oxide units. The mixture obtained was inertized with nitrogen and heated to  $95^\circ\text{C}$  with stirring with the aid of a pitched-blade stirrer ( $200 \text{ W/m}^3$ ). After the stirrer had been stopped, complete phase separation was awaited. The two-phase system was subsequently cooled with stirring to  $25^\circ\text{C}$  at  $1^\circ\text{C/min}$ . After the polyolefin particles had been separated with the aid of sieve, firm, particled were obtained, that show a broad DOD. These particles were dried in a vacuum stove at room temperature and a pressure of  $< 10 \text{ kPa}$ .

20 Comparative experiment C

In an Erlenmeyer flask 45 g of LDPE having a density of  $918 \text{ kg/m}^3$  and an M.I. of 8 dg/min was dissolved in 330 g of cyclohexane at about  $80^\circ\text{C}$  under reflux of the cyclohexane. 0.38 g of di-(ethyl benzylidene) sorbitol (being the product NC-4, supplied by Mitsui Toatsu) was added to the solution as nucleating agent. The solution was dosed to a beaker containing 750 g of water of about  $65^\circ\text{C}$ , to which 0.63 g of a surfactant (an alkane sulphonate having an average chain length of 14.5 C atoms) has been added. While the mixture was being stirred, with a power input of about  $200 \text{ W/m}^3$ , it was dispersed for 20 minutes, upon which a portion of the cyclohexane evaporated. Subsequently, the mixture was cooled to room temperature with an

average cooling rate of about 0.6 °C/min. The mixture was screened, so that strong, predominantly spherical gel particles with a particle size of about 2-3 mm were obtained. These particles were dried in a vacuum stove  
5 at room temperature and a pressure of <10 kPa. Porous polyethylene particles were formed.

Table 1Results of the examples

Example/ comp.exp	$\epsilon$ (%)	$E_{1a}$ (%)	$t_a$ (min)	DOD	D50 (mm)
I	43	116	1.2	0.32	1.9
II	40	95	0.8	0.31	3.4
III	36	106	0.7	0.23	1.6
IV	28	100	0.5	0.16	3.5
V	50	n.d.	n.d.	0.13	1.5
VI	47	102	0.8	n.d.	n.d.
VII	44	108	n.d.	n.d.	n.d.
VIII	45	n.d.	n.d.	0.23	3.7
IX	60	112	0.8	0.40	2.4
X	77	n.d.	n.d.	0.24	2.8
A	30	n.d.	0.7	0.76	n.d.
B	49	n.d.	0.8	0.47	5.9
C	61	n.d.	0.8	0.76	6.0

5

n.d. = not determined

C L A I M S

1. Process for preparing porous polyolefin particles,  
which process comprises the following steps:
  - 5           1) dissolving at least one cystallizable polyolefin in a solvent, in the absence of a nucleating agent, which results in the formation of a polyolefin solution,
  - 2) dispersing the polyolefin solution  
10           obtained in a non-solvent in the presence of a surfactant, at a temperature that is higher than the cystallization temperature of the polyolefin in the polyolefin solution, which results in the formation of a multi-phase  
15           system,
  - 3) cooling the resulting multi-phase system with stirring at a rate of between 0.05 and 10°C/minute to a temperature that lies below the cystallization temperature of the polymer  
20           in the polymer solution, so that firm polyolefin particles are formed,
  - 4) separating the polyolefin particles,
  - 5) drying the polyolefin particles.
2. Process according to Claim 1, characterized in  
25           that the dissolution and dispersion of the polyolefin in the solvent and non-solvent take place in a single step.
3. Process according to Claim 1 or Claim 2,  
characterized in that, before the multi-phase  
30           system is cooled, a portion of the solvent is evaporated from the multi-phase system formed.
4. Process according to any one of Claims 1-3, characterized in that the polyolefin is a polyethylene.



5. Process according to any one of Claims 1-3, characterized in that the polyolefin is a copolymer of ethylene and an  $\alpha$ -olefin.
6. Process according to any one of Claims 1-3, characterized in that the polyolefin is a polypropylene.
7. Process according to any one of Claims 1-6, in which the solvent is an n-alkane, i-alkane, cycloalkane, alkene, cycloalkene, a hydrogenated or non-hydrogenated aromatic compound, a polycyclic aromatic compound, chlorinated hydrocarbon or a mixture hereof.
8. Process according to Claim 7, characterized in that the solvent is cyclohexane, boiling point spirit, heptane or octane.
9. Process according to any one of Claims 1-8, characterized in that the concentration of the polyolefin in the polyolefin solution is between 10 and 35 wt.%.
10. Process according to any one of Claims 1-9, characterized in that the non-solvent is a polar compound when an apolar polyolefin is used.
11. Process according to Claim 10, characterized in that the non-solvent is water, acetone, methanol, ethanol or a mixture of these compounds.
12. Process according to any one of Claims 1-11, characterized in that the multi-phase system is cooled at a rate of between 0.1 and 5°C/min.
13. Process according to any one of Claims 1-12, characterized in that, during the drying, the partial pressure of the solvent in the vapour phase is less than 20% of the solvent's normal vapour pressure at the drying temperature.

14. Process according to Claim 13, characterized in that the drying is effected by means of a stripping gas.
15. Process according to any one of Claims 1-14, characterized in that a non-ionic surfactant is present.
16. Process according to Claim 15, characterized in that the non-ionic surfactant is an alkyl polyglycol ether or an ethoxylated fatty amine.
17. Porous polyolefin particles characterized in that the porous polyolefin particles meet the following requirements:
- A) a porosity of 5-85%
- B) an effective loadability  $E_{1A}$  of at least 95%, where

$$E_{1A} = \frac{\frac{\frac{m_A}{\rho_A}}{\frac{m_A}{\rho_A} + \frac{m_{PO}}{\rho_{PO}}}}{\text{porosity}} * 100\%$$

- C) an absorption time of at most 10 minutes
- D) the degree of dispersion of the particle size distribution is  $< 0.4$
- where  $E_{1A}$  is the polyolefin particle's effective loadability with an absorption agent,  $m_A$  the absorbed weight of the absorption agent,  $\rho_A$  the absorption agent's density,  $m_{PO}$  the weight of the porous polyolefin particles before absorption of the absorption agent and  $\rho_{PO}$  the density of the polyolefin.

18. Polyolefin particles according to Claim 17, characterized in that the porosity is 35-85%.
19. Polyolefin particles according to Claim 17 or Claim 18, characterized in that  $E_{1A} > 99\%$ .
- 5 20. Polyolefin particles according to Claim 17 or Claim 18, characterized in that the degree of dispersion is  $< 0.2$ .
21. Polyolefin particles according to any one of Claims 17-20, characterized in that the particles  
10 have been prepared from one polyolefin.
22. Polyolefin particles according to Claim 21, characterized in that the polyolefin has a DSC crystallization peak that is at least  $5^{\circ}\text{C}$  wide.
23. Polyolefin particles according to Claim 21 or  
15 Claim 22, characterized in that the polyolefin is LDPE.
24. Polyolefin particles according to any one of Claims 17-20, characterized in that the particles have been prepared from a mixture of polyolefins,  
20 one polyolefin in the mixture having a crystallization temperature that is higher than the crystallization temperature of the other polyolefin or polyolefins.
25. Polyolefin particles according to Claim 24,  
25 characterized in that the highest crystallization peak temperature is at least  $5^{\circ}\text{C}$  higher than the crystallization peak temperature of the other polyolefin or polyolefins.
26. Process for preparing porous polyolefin particles  
30 and use of the porous polyolefin particles as described and elucidated in the examples.
27. Use of porous polyolefin particles according to any one of Claims 17-25 or obtained according to the process according to any one of Claims 1-16 as

a concentrate, absorbent or carrier of additives  
that are to be released slowly and/or in a  
controlled manner.



Figure 1 SEM photograph of a porous polyolefin particle magnification 80x

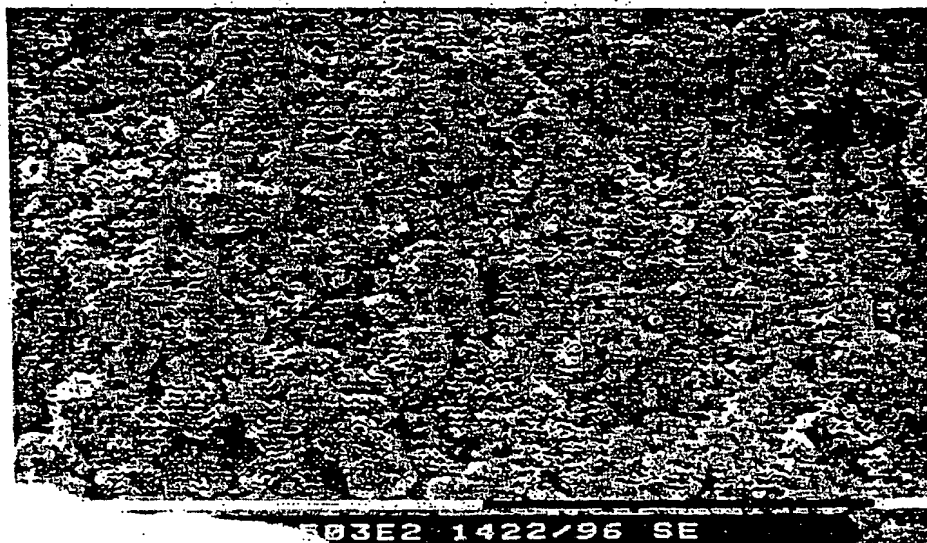


Figure 2 SEM photograph of a porous polyolefin particle magnification 500x

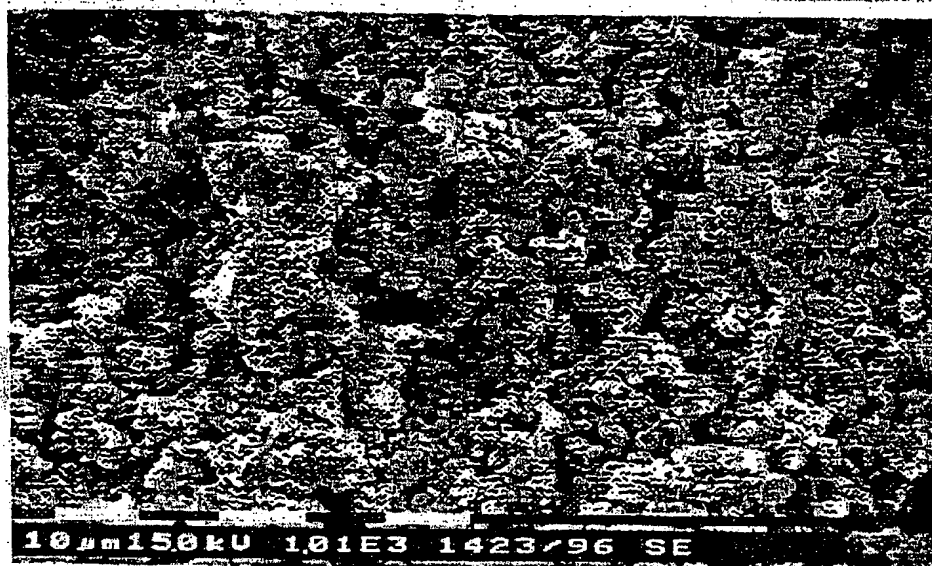


Figure 3 SEM photograph of a porous polyolefin particle magnification 1000x

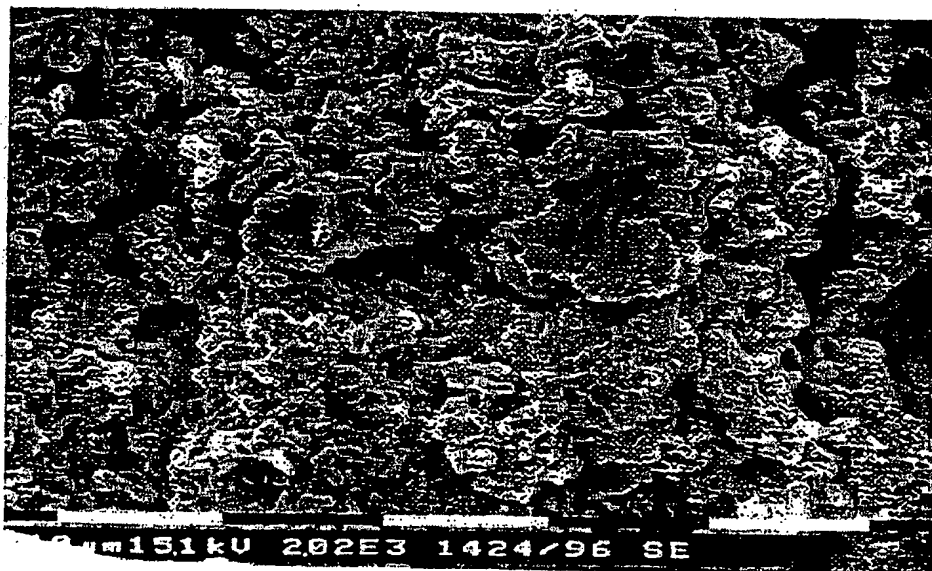


Figure 4 SEM photograph of a porous polyolefin particle magnification 2000x

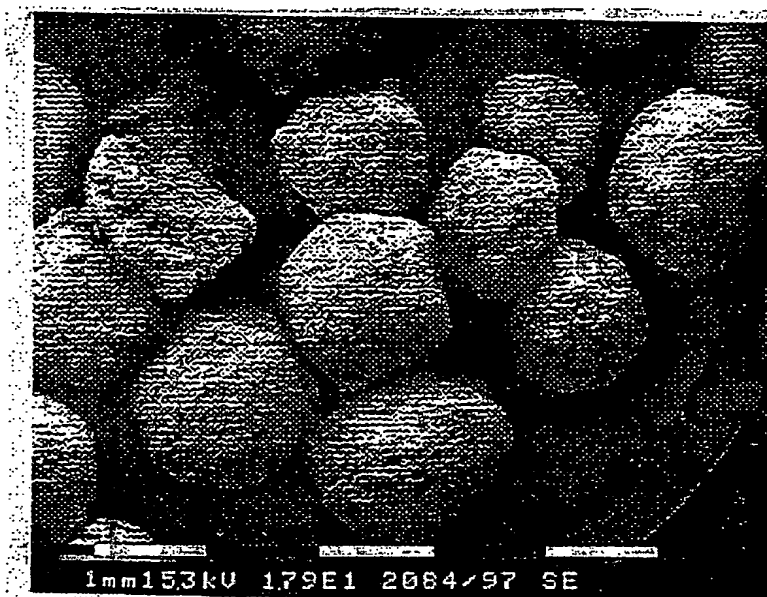


figure 5. SEM photograph of a porous polyolefin particle with a narrow DOD at a magnification of 18x (Example 1).

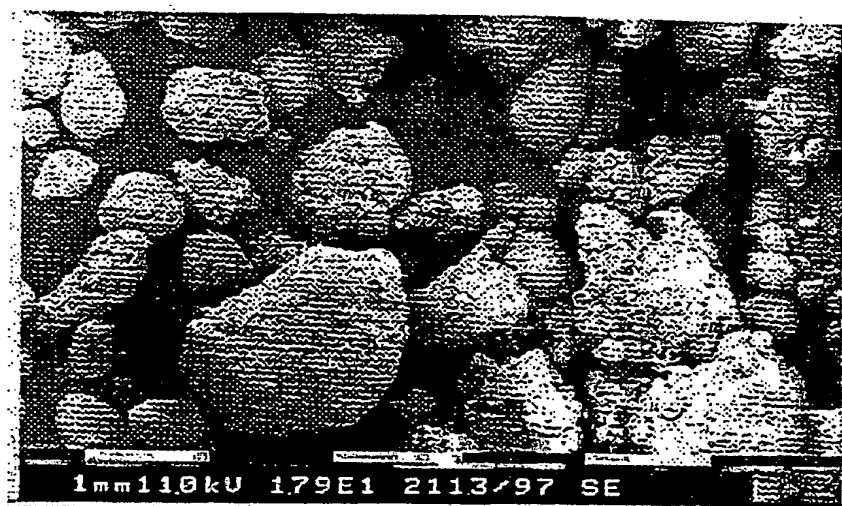


figure 6. SEM photograph of a porous polyolefin particle with a broad DOD at a magnification of 18x (Comparative Experiment C).

# INTERNATIONAL SEARCH REPORT

Int. l. Application No

PCT/NL 98/00321

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 C08J9/28 //A61K47/30

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 2 226 320 A (ICI PLC) 27 June 1990 see page 7, line 24 - page 8, line 4 see claims	1,4,9,12
P,X	WO 97 20884 A (DSM NV ; TABAKSBLAT RONALD (NL); AUSSEMS HENDRIKUS FRANCISCUS (NL)) 12 June 1997 see the whole document	1-27
A	EP 0 222 718 A (NILSSON KJELL G C ; MOSBACH KLAUS H (SE)) 20 May 1987	1-27
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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Date of the actual completion of the international search

4 September 1998

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Oudot, R



# INTERNATIONAL SEARCH REPORT

Int'l. Patent Application No.

PCT/NL 98/00321

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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